

Elevated mercury measured in snow and frost flowers near Arctic sea ice leads

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[1] Elevated mercury concentrations have been reported in arctic coastal snow far from emission sources. The mercury is deposited during mercury depletion events (MDEs), a set of photochemical atmospheric reactions involving reactive halogens. The highest mercury concentrations are clustered near the coast, leading to speculation that sea ice or sea ice leads play a role in MDEs. The nature of this connection is not fully understood. We report mercury concentrations up to 820 ng/L in snow and frost flowers along sea ice leads near Barrow, Alaska. These concentrations are nine times higher than values from nearby coastal snow and are almost half of the mercury maximum contaminant level in United States drinking water. The high values were found only near leads that had convective plumes above open water suggesting that the same processes that produce a supersaturated environment for water vapor near sea ice leads may be instrumental in mercury deposition.

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1. Introduction

[2] In the Arctic during mercury depletion events, gaseous elemental mercury (GEM) in the lower troposphere is transformed into potentially bioavailable reactive gaseous mercury (RGM) through a unique series of photochemical reactions [Schroeder *et al.*, 1998; Ariya *et al.*, 2002; Skov *et al.*, 2004]. Concentrations of Hg in snow increase from typical background levels of 1–8 ng/L [Lu *et al.*, 2001; Douglas and Sturm, 2004] to 100 ng/L [Lindberg *et al.*, 2002]. Meanwhile surface ozone (O₃) concentrations decrease to below 10 ppb [Schroeder *et al.*, 1998]. It is widely thought that the GEM-to-RGM transformation occurs only when halides, predominantly Br[−] [Hausmann and Platt, 1994], are activated to create halogens and halogen oxide radicals that act as catalysts [Foster *et al.*, 2001]. The halogen source is believed to be linked to

seawater or sea ice, with aerosols from open ocean water [Lindberg *et al.*, 2002; Vogt *et al.*, 1996], or snow and ice surfaces on sea ice [Kaleschke *et al.*, 2004], two possibilities. Regardless of the source, it is established that MDEs take place in the lower troposphere of the Arctic [Barrie and Platt, 1997; Bottenheim *et al.*, 2002].

[3] We reasoned that if we compared the mercury concentration of snow and ice near open leads to snow obtained elsewhere, the results would suggest if leads played a role in mercury deposition. Samples were collected from one large and one small lead in the Beaufort Sea north of Barrow, Alaska (Table 1). The smaller lead was about 20 meters wide and had no visible vapor plume above it. The larger lead was over 200 meters wide and had a dark gray convective vapor plume above it at both times it was sampled (Figure 1). Vapor plumes form when the strong thermal contrast between warm sea water (−2°C) and cold (−30°C) arctic air generate convection cells [Alam and Curry, 1995] that drive vapor transport upward from the lead into a stably stratified lower atmosphere. As a result of this vigorous transport the near-surface air over sea ice in which there are leads is often supersaturated with respect to water vapor [Andreas *et al.*, 2002].

2. Site Locations and Results

[4] Our samples included seawater from open leads, frost flowers from newly formed sea ice, surface hoar from snow on ice floes within 100 meters of leads, and surface snow several kilometers inland and upwind of the leads. Two of the ice crystal types we sampled, frost flowers [Perovich and Richter-Menge, 1994] and surface hoar [Colbeck, 1988], grow directly from water vapor in the air. Frost flowers are delicate ice crystals with different shapes ranging from needles to platelets depending on the air temperature in which they form [Perovich and Richter-Menge, 1994; Martin *et al.*, 1996]. They are commonly observed on thin ice skims that form over open sea ice leads. These skims include fractionated seawater transported vertically through ice grain boundaries toward the cold upper surface by a phenomenon called the thermomolecular pressure gradient [Martin *et al.*, 1996]. Surface hoar is also a delicate vapor phase form, consisting of thin upright blade-like crystals that plate out on snow and other cold surfaces. We found both types of vapor phase crystals to be common near leads but completely absent on land, suggesting that the temperature gradient above leads provides a moisture source that produces these crystals.

[5] Our frost flowers had a similar chemical composition to those from Antarctica [Rankin *et al.*, 2002] with elevated salinity (60–120 psu) compared to seawater (35 psu), no enhancement in bromide compared to chloride, and sulfate

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Table 1. Summary of the Sample Locations and Hg Concentrations From This Study

Lead Type	Location	Date	Weather	Crystal Description	Crystal Age	#Samples	Hg $\pm 1\sigma$ (ng/L) ^{a,b}
20 meter wide	72.37°N, 149.82°W	4/10/03	Clear skies, -20°C	Frost flowers	<12 hours	1	14
				Seawater		1	4
				Reference snow 20 m upwind	Many days	1	106
200 meter wide	71.36°N, 156.73°W	3/1/04	Clear skies, -26°C	Frost flowers	<4 hours	3	181 \pm 8
				Frost flowers	<8 hours	3	154 \pm 17
				Frost flowers	<8 hours	3	185 \pm 32
				Surface hoar on ice block 50 m upwind	~2 days	3	421 \pm 31
				Seawater		1	1.5
				Reference snow 5 km southeast	Many days	1	37
10 kilometer wide	71.37°N, 156.68°W	5/8/04	Clear skies, -12°C	Hoar frost	~11 days	2	820 \pm 160
				Reference snow 15 km southeast	Many days	3	91 \pm 39

^a σ = standard deviation when two or more samples were analyzed.

^bMercury analyzed by Cold Vapor Atomic Fluorescence Spectrophotometry.

depletion. However, the most significant result of this study is that ice crystals from the vicinity of leads yield mercury concentrations almost an order of magnitude greater than any published from polar snow or ice samples to date (Figure 2) [Lu *et al.*, 2001; Lindberg *et al.*, 2002].

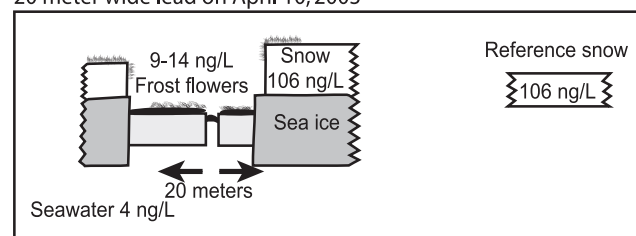
[6] Significantly depleted ozone and GEM concentrations measured in Barrow while we sampled indicate our snow and frost flowers were collected during periods when MDEs were in progress above the Barrow atmospheric monitoring site 10 km to the southeast. However, there is little connection between the strength of the MDE as measured by lower tropospheric air composition at Barrow

and the concentration of Hg found in the snow and ice near leads (Figure 3). For example, six days prior to our sampling of frost flowers at the smaller lead the chemical composition of the air at Barrow was that typical of an MDE [Lindberg *et al.*, 2002]. Snow a hundred meters from the lead that was exposed for six days during the active MDE at Barrow yielded a Hg concentration of 106 ng/L. In contrast, 12 hour old frost flowers yielded concentrations of 14 ng/L. A possible interpretation of these data is that the MDE was depositing Hg to the snow at a relatively slow or episodic rate. Hence the young frost flowers were low in Hg while the distal snow, exposed longer, was higher in Hg. Mercury concentrations from the plumeless lead appeared not to have been related to the Hg concentration in reference terrestrial snow.

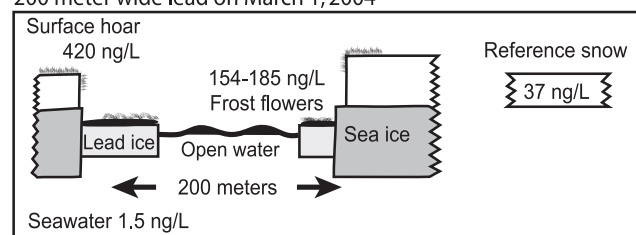


Figure 1. Photographs of the two leads investigated in this study. The small lead was roughly 20 meters wide (top) and the large convective lead was 200 meters wide with an extensive shelf of nilas (bottom). Frost flowers and surface hoar are visible in both images.

20 meter wide lead on April 10, 2003



200 meter wide lead on March 1, 2004



200 meter wide lead (opened to 10 kilometer wide) on May 8, 2004

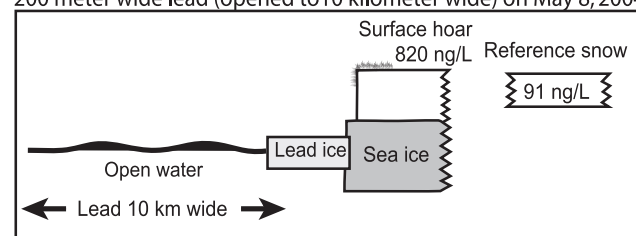


Figure 2. Schematic cross section of the leads and snow and ice sample locations in this study.

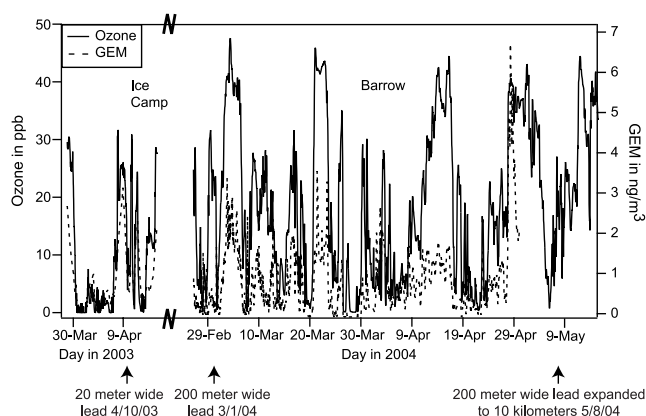


Figure 3. Plot of ozone and GEM concentrations in air for the timeframe in 2003 and 2004 during which samples were obtained. GEM concentration measurements are not available after April 29, 2004.

[7] Conditions were markedly different at the large lead. On March 1, 2004 when we visited it, an MDE had been underway at Barrow for at least 4 days. Snow sampled the same day on land 15 km to the east of the lead had a Hg concentration of 37 ng/L, consistent with MDE deposition [Lu *et al.*, 2001; Lindberg *et al.*, 2002]. At the lead, despite the fact that it was a bright sunny day (temperature of -22°C), diamond dust was crystallizing in the air and falling back onto the lead and the surrounding floes. The source of the dust was the convective plume rising above the lead. Two generations of frost flowers were present on the 10-meter wide strip of nilas (young ice) that was actively forming along the lead margins. The youngest flowers, located one meter from the lead edge, were no more than four hours old and yielded Hg concentrations of 181 ± 8 ng/L. Older frost flowers (8 hours old) five meters from the lead edge had Hg concentrations that ranged from 154 ± 17 to 185 ± 32 ng/L. Still older crystals, in this case bladed surface hoar from a thick floe next to the lead, had a value of 421 ± 31 ng/L. According to local seal hunters who frequent the leads, this particular lead had been open and actively forming nilas ice for the previous five days.

[8] The larger, 200 m wide lead, was revisited on May 8th after it had opened to over 10 km wide. Surface hoar located atop a 1-meter high ice block 25 meters inward from the lead edge yielded a Hg concentration of 820 ± 160 ng/L. This value is higher than any published Hg concentration for arctic or Antarctic snow. On the same day the large lead sample was obtained, snow on land 15 km from the lead had a Hg concentration of 91 ± 39 ng/L. Based on a series of images at 250 meter resolution from the MODerate resolution Imaging Spectroradiometer (MODIS; <http://sv.gina.alaska.edu/barrow.html>) we estimate that the large lead complex generated a plume for 20 days between March 1 and May 8.

3. Summary and Discussion

[9] Mercury concentrations from frost flower and snow samples obtained near leads in the Arctic Ocean yield three results. First, frost flower and surface hoar snow adjacent to leads contain Hg at elevated concentrations previously

unreported in the literature. This Hg appears to be uncorrelated with both the MDE chemistry reported at regional monitoring locations on the coast (like the NOAA Climate Monitoring and Diagnostics Laboratory 8 km east of Barrow) and with reference snow samples obtained 15 km from the leads. Furthermore, the Hg concentrations are far higher than the ~ 100 ng/L maximum Hg concentrations in snow usually associated with MDEs [Lu *et al.*, 2001; Lindberg *et al.*, 2002]. This result suggests an enhancement of Hg deposition near leads. Second, the Hg deposition near leads is rapid and may be cumulative, producing surprisingly high values in the span of a few hours. Four-hour-old frost flower crystals had Hg concentrations that were almost twice that expected for MDE deposition to snow on land. Surfaces exposed to an active lead for over 20 days yielded concentrations almost eight times that of snow exposed to a typical MDE. Third, anomalously high Hg concentrations are associated with the large lead that had a convective plume. This may be due to local meteorological conditions around the leads or because large leads generate convection cells above them [Alam and Curry, 1995]. The convective cells transport vapor from the seawater surface to the lower atmosphere. Some of this vapor is deposited near the lead as diamond dust, frost flowers and surface hoar. Convective mixing extends vertically for several kilometers above leads [Shepson *et al.*, 2003] and thus could affect MDE chemistry in the vicinity of leads. Without detailed measurements of the meteorological conditions and halogen concentrations above leads the effect of convection on depositing Hg to snow and ice near large leads cannot be ascertained.

[10] Two mechanisms could link the convective plume above large leads with Hg deposition:

[11] 1. Mercury concentrations could be enriched if the convective processes and/or meteorological conditions near leads promoted the transfer of halogens from seawater or frost flowers or sea ice to the air above the lead. The GEM-to-RGM transformation could thus be enhanced in and around the plume due to an abundance of reactive halogens.

[12] 2. Alternatively, or in concert with halogen enhancement near open leads, scavenging of Hg from the air could be more efficient near the supersaturated air plume where diamond dust is often falling. Frost flowers and surface hoar crystals present a large specific surface area (300 to 590 g/cm^3 [Legagneux *et al.*, 2002]) that may make them a more efficient scavenger of dry-deposited Hg than other, less ornate snow crystals. Since these crystals grow from the vapor phase they are more prevalent near leads with plumes.

Careful measurements of meteorological conditions above a lead and of BrO above and away from leads would answer whether the mechanism is chemical (1 above) while detailed measurements of halogen and Hg concentrations and SSA values from frost flowers, surface hoar and diamond dust along transects heading away from leads would answer whether the mechanism is physical (2 above). Local and regional meteorological conditions would have to be assessed in order to determine whether halogens or RGM can be efficiently exported from leads with aerosol particles or with snow or ice crystals (frost flowers, surface hoar, sea ice).

[13] Heat transfer and the development of convective vapor plumes above leads is relatively well understood

[Alam and Curry, 1995; Glendening, 1995], but the export of moisture and halogen species from leads, and their role in Hg deposition, is not. For example, the thermal contrast between ambient air and surface seawater temperatures may control whether surface hoar or frost flowers near a lead will have elevated Hg concentrations. We need to understand how these processes are coupled because the size, density and persistence of off-shore leads could play an important role in controlling mercury deposition near leads. This could affect MDEs on a regional scale. Moreover, a changing climate is altering the nature, extent, and duration of sea ice in the Arctic and Antarctic [Rothrock et al., 1999]. These widespread changes will undoubtedly affect the formation of leads in myriad ways and, in turn, are likely to affect the relationship between leads, MDE chemistry and the deposition of Hg.

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